

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Inventor: Johannes Bos Group Art Unit: 1796
Application No.: 10/580,018 Examiner: G. LISTVOYB
Filed: May 19, 2006 Docket No.: 127898

For: PROCESS FOR MAKING DAPBI-CONTAINING ARAMID CRUMBS

DECLARATION UNDER 37 C.F.R. §1.132

I, Johannes Bos, a citizen of The Netherlands, hereby declare and state:

1. I have a degree as engineer in HTS-Chemistry, which was conferred upon me by Van't Hoff Instituut in Rotterdam, The Netherlands in 1984.

2. I have been employed by Teijin Aramid (formerly named Akzo, Akzo Nobel and Teijin Twaron), the Netherlands, since 1989 and I have had a total of 19 years of work and research experience in the field of aramid polymers for use in fiber spinning processes, as well as a range of other topics related to polymer science and engineering.

3. I am a named inventor in the following patents in this field: U.S. Patent No. 6,355,094; U.S. Patent No 5,776,354; U.S. Patent No 5,750,030; U.S. Patent No 5,738,791; WO 2008/028605 and WO 2008/061668.

4. I am a named inventor in the above-captioned patent application. I am familiar with the patent application.

5. I am employed by the Assignee, Teijin Aramid, of the above-identified

patent application. In the course of my employment, I receive compensation for my work relating to research and development regarding aramid polymers for use in fiber spinning processes. I am not being specially compensated for my work in preparing this Declaration.

6. The following experiments were included in internal records of Teijin Aramid. I have read and understood write ups of the experiments in these records and below is my opinion regarding these experiments.

I. In Making A Crumb As Recited In Present Claims 1 And 10. The Use Of Lithium Chloride And Calcium Chloride Is Not Equivalent

In the Office Action, I understand the U.S. Patent Office to allege that Chernykh, RU 2,017,866, indicates the use of lithium chloride and calcium chloride to be equivalent. See Office Action, page 3. Chernykh mentions the use of "CaCl₂ or LiCl" without any reference to make clear what the "or" actually means. The use of the word "or" does not necessarily mean that when CaCl₂ is changed for LiCl, all properties and effects remain the same. For instance, the viscosity of the polymer solution, relative viscosity of the polymer, flow behavior of the polymer solution etc. can be different. See the experimental results further in this declaration. Thus "or" does not mean that both salts are exchangeable without changing at least some of the results and effects.

In addition Chernykh relates to polymer solutions (page 4, column 2). Addition of CaCl₂ or LiCl both enhances the dissolving power. The exchangeability of CaCl₂ and LiCl as disclosed by Chernykh only relates to conditions to obtain polycondensate solutions that are suitable for extrusion and fiber spinning (page 4, col. 2). However, lithium chloride and calcium chloride behave differently when making an

aramid crumb, and cannot be interchanged successfully as alleged by the examiner.

Four sets of polymerization experiments were conducted to show that calcium chloride and lithium chloride are not equivalent as compounds for forming aramid crumb.

A. First Set Of Experiments

The first set of experiments consisted of reproducing the traditional approach of forming a standard aramid poly-para-phenyleneterephthalamide (PPTA) crumb using p-phenylenediamine (PPD) and terephthaloyl dichloride (TDC) as the monomers. These experiments included taking ground and dried calcium chloride and stirring it into a reaction vessel (Waring Blender with a cooled bottom) containing N-methyl pyrrolidone (NMP) as the solvent.

The mixture of calcium chloride and NMP was continuously stirred during thermostating to 0 °C in order to obtain a finely divided suspension. Subsequently, PPD, distilled in vacuo (b.p. 168 °C/18 mm) and ground, was added and the mixture was continuously stirred. Shortly afterwards, molten TDC (distilled in vacuo, b.p. 136 °C/10 mm) was rapidly added from a dropping funnel to form a reaction mixture. The reaction mixture was heated with an IR lamp and vigorously stirred to prevent solidification. After about a minute, the reaction mixture formed a semi-solid material that separated into crumbs when the inherent viscosity (η_{inh}) of the polymer exceeded a value of about 3.

Table 1 illustrates the reaction conditions of the above experiment using different weight percentages of calcium chloride and the monomers (i.e., PPD and TDC). The resulting crumbs were coagulated with water, washed and then dried.

Table 1: Inherent Viscosity of First Set of Experimental Trials

Experiment No.	ml NMP	CaCl ₂ , wt% ¹	PPD and TDC monomer concentration, wt% ²	η_{inh}
1	200	15.25	11.84	4.05
2	200	5.66	9.09	3.05
3	200	7.41	8.94	3.15
4	200	9.09	8.79	4.05
5	200	10.71	8.65	4.02
6	200	12.28	8.51	5.05
7	200	16.67	8.12	4.6
8	200	20.00	7.82	3.8
9 *	40000	10.91	7.94	5.33

¹ wt(CaCl₂)/(wt(CaCl₂)+wt(NMP))*100.

² wt(monomers)/wt(total mixture)*100.

* performed in a 160 L reactor.

As shown above in Table 1, a PPTA crumb was formed from a relatively low monomer concentration in the NMP/calcium chloride mixture and the inherent viscosity (η_{inh}) of the PPTA polymer was always greater than 3.

B. Second Set Of Experiments

A second set of experiments was performed in exactly the same manner as the first set of polymerization experiments, except that the CaCl₂ was replaced with CaBr₂, BaCl₂, CaSO₄, MgCl₂, ZnCl₂, Zn(OAc)₂, NH₄Cl, or LiCl, in the range of 3 – 15 wt%. The results for this second set of experimental trials are summarized below in Table 2.

Table 2: Inherent Viscosity of Second Set of Experimental Trials

Salt	Salt Concentration %	Monomer Concentration %	η_{inh}
CaBr ₂	10.71	8.65	0.73
CaSO ₄	10.71	8.65	0.39
MgCl ₂	2.91	9.33	0.44
MgCl ₂	5.66	9.09	0.56
MgCl ₂	8.26	8.86	1.39
MgCl ₂	10.71	8.65	0.95
MgCl ₂	13.04	8.44	0.44
ZnCl ₂	2.91	9.33	0.48
ZnCl ₂	5.66	9.09	0.58
ZnCl ₂	8.26	8.86	0.64
ZnCl ₂	10.71	8.65	0.59
ZnCl ₂	13.04	8.44	0.39
NH ₄ Cl	10.71	8.65	0.28
LiCl	10.71	8.65	0.30
BaCl ₂	10.71	8.65	0.29
Zn(OAc) ₂	9.91	8.72	0.19

As shown above in Table 2, the η_{inh} for a low monomer concentration using salts other than calcium chloride ranged from 0.19 to 1.39, which as described above, is too low of an inherent viscosity to form a crumb. Furthermore, the addition of LiCl only resulted in an inherent viscosity of 0.30, whereas as shown above, the addition of calcium chloride unexpectedly achieved a substantially greater inherent viscosity that enabled crumb formation.

C. Third Set Of Experiments

The third set of experiments consisted of a large number of polymerization reactions using a relatively high monomer concentration of PPD and TDC and using CaCl₂, LiCl, LiBr, MgCl₂ and MgBr₂ as the salts.

More specifically, the procedure for this third set of experimental trials consisted of charging an oven-dried reactor to a temperature of 60 °C, wherein the reactor contained:

450 mL (461.7 g) of NMP and 14.80 g of salt. The reactor was then flushed with nitrogen gas for 15 minutes to dissolve the salt under stirring. After cooling the reactor to 20 °C, 37 grams of PPD were added followed by the addition of 69.44 grams of TDC. The TDC was either

(1) added to the mixture at once or (2) added in ten equal portions of 6.944 g.

If ten equal portions of the TDC were added to the mixture, the time between the addition of each portion of TDC was about 3 to 5 minutes and the temperature of the mixture increased after the addition of each portion of TDC.

After all portions of the TDC were added to the mixture, the mixture was stirred for 1 hour and 16.35 g of the indicated salt as powder were added to form the resulting mixture that coagulated into a slurry upon the addition of water. The slurry was filtrated over a glass filter and the polymer was dried in vacuo for 16 hours at 110 °C. The η_{inh} for each of the polymers was determined, and the results are summarized below in

Table 3.

Table 3: Inherent Viscosity of Third Set of Experimental Trials

Exper. No.	PPD (grams)	TDC (grams)	Number of portions of TDC Added	Monomer Conc. (wt%)	Salt	Salt Conc. (wt.%)	End temp °C	Solvent	η_{inh}
1	37.00	69.44	1x	18.26	CaCl ₂	3.11	-	NMP	0.57
2	37.00	69.44	10x	18.26	CaCl ₂	3.11	74	NMP	0.43
3	37.00	69.44	10x	18.26	CaCl ₂	3.11	58	NMP	0.46
4	37.00	69.44	1x	18.26	CaCl ₂	3.11	56	NMP	0.63
5	37.00	69.44	10x	18.26	LiBr	3.11	58	NMP	0.38
6	37.00	69.44	10x	18.26	LiCl	3.11	60	NMP	0.57
7	25.82	48.15	5x	13.51	LiCl	2.19	60	NMP	0.41
8	37.00	69.44	10x	18.26	MgCl ₂	3.11	56	NMP	0.31
9	37.00	69.44	10x	18.26	MgBr ₂	3.11	60	NMP	0.30

As shown above in Table 3, each of the experimental trials, comprised of PPD, TDC, NMP and one of the various salts (including CaCl₂), had an η_{inh} value between 0.38 and 0.63. As the final products for this third set of experimental trials formed a turbid yellow to a brown syrupy mass, a crumb could not be formed from any of these experiments.

With regards to CaCl₂, the major difference between these experiments and the experiments of Table 1 is the monomer and the salt concentrations. In this case the amount of salt was too low and the amount of monomer too high to keep the polymerization going on.

Various LiCl concentrations and monomer concentrations were used as well, however, in none of the cases crumb was formed and no polymer with sufficiently high molecular weight was obtained.

D. Fourth Set Of Experiments

The fourth set of experiments repeated the same conditions as the first and second set of experiments. Here, the LiCl and CaCl₂ salt were added to the TDC/PPD mixture with either dimethyl acetamide (DMAc) or NMP as solvent. The η_{inh} for the fourth set of experiments is shown below in Table 4.

Table 4: Inherent Viscosity of Fourth Set of Experimental Trials

Solvent	Salt	Salt wt%	Monomer Concentration (weight %)	Appearance of Mixture	η_{inh}
DMAc	LiCl	0.50	9.54	Custard-like	0.89
		0.99	9.50	Custard-like	0.90
		2.91	9.33	Custard-like	0.78
		5.66	9.09	Custard-like	0.32
NMP	LiCl	0.50	9.54	Custard-like	0.28
		0.99	9.50	Custard-like	0.69
		2.91	9.33	Custard-like	0.74
		5.66	9.09	Custard-like	0.26
DMAc	CaCl ₂	0.99	9.50	Custard-like	0.24
		1.96	9.41	Custard-like	0.50
		2.91	9.33	Custard-like	1.05
		5.66	9.09	Custard-like	1.52
		8.26	8.86	Custard-like	1.56
		10.71	8.65	Custard-like	1.36
NMP	CaCl ₂	10.7	8.65	crumb	4.27* 4.04 4.31

*: Analysis performed in triplicate

As shown above in Table 4, the NMP/CaCl₂ solvent/salt combination had an η_{inh} value of 4.31, while the remaining solvent/salt combinations, including NMP/LiCl, only gave low molecular weight materials wherein the highest η_{inh} value was 1.56 (for DMAc/CaCl₂). As such, only the NMP/CaCl₂ solvent/salt combination obtained η_{inh} value

which was high enough to form a crumb.

The publication of E. Chodkowski (Polimeri, 1971, 514-515; English translation added as Annex) mentions the use of LiCl and CaCl₂ for the preparation of PPTA in DMAc. In case the salt concentration is between 0.5 – 1 mole/L the reduced viscosity (η_r) of PPTA with CaCl₂ is always significantly higher than η_r obtained with LiCl. Crumb formation is not disclosed (Table 5).

Table 5

Salt	Conc. salt, mole/L	Reduced viscosity
LiCl	0.5	0.808
LiCl	0.75	0.555
LiCl	1.00	0.372
CaCl ₂	0.50	1.539
CaCl ₂	0.75	1.273
CaCl ₂	1.00	0.497

E. Conclusions

The above results show that the formation of PPTA from TDC and PPD using CaCl₂/NMP solutions renders sufficient inherent viscosity (i.e. sufficient molecular weight). In case of LiCl the inherent viscosity is significant lower. As such, the above evidence confirms that the use of a CaCl₂/NMP salt/solvent combination for forming an aramid crumb is the exception. The rule is that no crumb is formed, as has been demonstrated by the use of other salt/solvent combinations, such as the LiCl/NMP salt/solvent combination.

F. Fifth Set Of Experiments

The fifth set of experiments relates to DABPI-containing aramids. With regard to aramids based on PPD, DAPBI and TDC, the situation is even more extreme. No documents were found that disclose the formation of crumbs with these DABPI-containing aramids. All published documents disclose that the polymer was obtained as a solution. These documents also suggested adding solubility promoting salts i.e. CaCl_2 or LiCl , to improve the solubility of the aramid in the solvent. See further also III.

In Table 6 below some comparisons are made between experiments 1 and 2 as performed by the R&D of Teijin Aramid and reference data from the prior art showing the results in different solvent systems and of different copolymer compositions.

Table 6

Experiment	Amines	Composition %	Solvent	Salt	b.c.	Appearance
1	PPD/DAPBI	50/50	NMP	CaCl_2	400	solution
2	PPD/DAPBI	50/50	NMP	LiCl	150	solution

Reference	Amines	Composition %	Solvent	Salt	b.c.	Appearance
Chernykh; example 1	Cl-PPD/DAPBI	40/60	DMAc	LiCl	179	solution
Chernykh example 4	Cl-PPD/DAPBI	80/20	DMAc	LiCl	62	solution
Chernykh example 7	PPD/DAPBI	70/30	DMAc	none	0	solution
Nakagawa US 4,018,735 example 4	PPD/DAPBI	90/10	NMP/HMP ¹	LiCl	50	semi-transparent
Yung example 8	PPD/DAPBI	40/60	NMP	none	0	solution
Mera US 4,172 938 example 34	PPD/DAPBI	80/20	NMP	CaCl_2	39	powder (see Table 8)

¹ hexamethylenephosphoramide

In view of the fact that those of ordinary skilled in the art have not succeeded in forming PPTA crumbs using NMP/LiCl instead of NMP/CaCl₂, it is understood that NMP/LiCl will not give crumbs in DAPBI-containing aramid polymers. This has been confirmed by Example 4 of U.S. Patent No. 4,018,735 (Nakagawa), detailing the formation of a semi-transparent aramid dope from the reaction of PPD, DAPBI, TDC and a NMP/LiCl solvent and by Example 34 of U.S. Patent No. 4,172 938 (Mera) disclosing the formation of a powder (see Table 8).

7. I have conducted the following experiments.

II. Crumbs Are Obtained When Using The Conditions Recited In Present Claims 1 And 10

As described above, the copolymerization of PPD and TDC leads to an aromatic polyamide (PPTA) in the form of a crumb. Such crumbs are known and highly desired because they can be easily purified and possess a high processability for an extruder in a large scale commercial process. However, the present application embodies the scenario when a portion of PPD has been replaced with 5(6)-amino-2-(p-aminophenyl)-benzimidazole ("DAPBI"). Such compounds were found to form a solution, powder or gel, which has been a serious problem for large-scale production of a DAPBI-containing aramid.

To demonstrate the difficulty in obtaining a crumb from a DAPBI-containing polymer, I have performed two additional sets of experiments to show that crumbs are formed if the components and conditions recited in present claims 1 and 10 are satisfied.

The sixth set of experiments is represented as Examples 1-7 as described on page 5 of the present specification and the seventh set of experiments is represented as Comparative Examples 1-5 also described on page 5 of the present specification.

A. Sixth Set Of Experiments

The sixth set of experiments included pre-drying a 2L flask for 1 hour in an air circulation oven at 120 °C. Subsequently, the 2L flask was connected with a mechanical stirrer, an N₂ inlet and outlet stream between about 40 - 60 mL/min, and a vacuum supply. 400 mL of the NMP solvent containing 10.4 weight percent of CaCl₂ was combined with an amine mixture comprised of 90 mole percent PPD and 10 mole percent DAPBI and placed in a reactor. The flask was sealed and purged two times with nitrogen gas. After the amine mixture/NMP solvent were stirred for 30 minutes at 150 rpm, heated to 60 °C and mixed for 0.5 hours to dissolve or disperse the amines into the NMP solvent, the flask was cooled with a coolant to 5-10 °C. After removing the coolant, the stirrer velocity was increased to 320 rpm and 100 mole percent of TDC were introduced into the flask with a funnel. After the flask and the funnel were rinsed with 50 mL of the NMP solvent, the flask was closed and the mixture was allowed to react for at least 30 minutes. The whole reaction mixture spontaneously turned into a crumb. Such "crumb-particle" comprises polymer, solvent, salt, HCl and remaining monomers and oligomers. During reaction the monomer and oligomer concentrations diminish, so that when the process is stopped a crumb particle consists essentially of NMP, CaCl₂, HCl and polymer.

This aramid crumb was combined with demi-water in a Condux LV15 coagulator allowing the mixture to coagulate and was then collect on a RVS filter. The coagulated

crumb product was then washed four times with 5L of demi-water to remove the solvent, CaCl_2 and HCl and the washed product was collected in a 2L glass beaker and dried in vacuum for 24 hours at 80 °C.

Finally, the coagulated crumb was dissolved in sulfuric acid to form a solution to determine the relative viscosity and the inherent viscosity of the aramid crumb/sulfuric acid solution at 25 °C in an Ubbelohde viscometer. The above experiment was repeated six times with different mole percents of PPD and CaCl_2 . The results of each of these seven experiments are summarized below in Table 7.

Table 7: Process Conditions for Experiments 1-7

Experiment	PPD (a) mole%	DAPBI (b) mole %	CaCl_2 (c) wt%	b.c	η_{rel}	η_{inh}	Appearance
1	90	10	10.40	104.0	6.29	6.46	crumb
2	90	10	11.55	115.5	5.93	6.2*	crumb
3	80	20	9.85	197.0	5.38	5.92	crumb
4	80	20	10.28	205.6	4.10	5	crumb
5	60	40	4.77	190.8	5.69	6.01	crumb
6	33	67	3.09	207.0	6.98	6.45	crumb
7	30	70	2.82	197.4	6.2*	6.3*	crumb

average of 3 values

* calculated value

As shown above in Table 7, Experiments 1-7 each contain amounts of DAPBI ranging from 10 to 70 mole% and amounts of calcium chloride ranging from 2.82 to 11.55 wt%. Furthermore, each of the compositions described in Experiments 1-7 formed a crumb.

B. Seventh Set Of Experiments

The seventh set of experiments consisted of five comparative experiments. Comparative Experiments I-IV were performed under the same conditions as Experiments 1-7 in the sixth set of experiments, except that the amounts of DAPBI and calcium chloride were changed. Comparative Experiment V was performed in the same manner as described in U.S. Patent No. 4,172,938. Below Table 8 illustrates the results of the second set of experiments.

Table 8: Process Conditions for Comparative Experiments I-V

Comparative Experiments	PPD (a) mole%	DAPBI (b) mole %	CaCl ₂ (c) wt. %	b.c	η_{rel}	η_{inh}	Appearance
I	80	20	11.55	231.0	4.59	5.3	dough/paste
II	60	40	5.49	219.6	5.87	6.2	dough/paste
III	33	67	4.56	306.9	2.75	3.58	dough/paste
IV	33	67	2.88	193.0	2.31	3.04	gel
V	80	20	1.96	39.2	1.56	1.93	powder

The difference of comparative experiment IV of Table 8 and experiment 6 of Table 7 is the formation of a gel rather than a crumb, which is quite sensitive on the CaCl₂ concentration. If a gel is formed, then there is no further mixing and as a result movement of the reactive ends of the polymer to each other is inhibited whereby the reaction rate considerably drops thereby resulting in low molecular weight material.

As shown above in Table 8, when the mole percent of DAPBI (b) changes within the range from 20 to 67 mole% and the weight percent of calcium chloride (b) within the range from 1.96 to 11.55 wt%, no crumb is formed but a dough/paste, gel or powder, which are unsuitable for forming aramid fibers and films on a commercial scale. These data demonstrate that although the individual ranges of DAPBI and calcium chloride as

shown in Table 8 are similar to the ranges of Table 7, the relation between these values as expressed by the mole percent of DAPBI (b) multiplied by the weight percent of calcium chloride (c) is essential for the question whether or not a crumb will be formed.

C. Conclusion

It can therefore be concluded that replacing a portion of the PPD monomer with DAPBI in NMP/CaCl₂ under reaction conditions that are different from the conditions recited in claims 1 and 10 of the above-identified application as indicated in Table 8, will not form a crumb. In other words, crumbs can be obtained using this system, but a very specific relationship between the amounts of DAPBI and of CaCl₂ is required, which conditions are recited in the claimed subject matter.

III. Deficiencies Of Cited References

8. I have further read and understood the three references U.S. Patent No. 4,308,374 ("Vollbracht"), RU 2,017,866 ("Chernykh ") (English translation) and U.S. Patent No. 5,646,234 ("Jung") cited by the U.S. Patent Office in the Office Action.

Below are my comments regarding each of these references.

Vollbracht, Jung and Chernykh teach away from the subject matter described in present claims 1 and 10. Vollbracht describes a method of producing PPTA using PPD and TDC in a NMP/CaCl₂ solvent/salt combination, wherein the method directly polymerizes PPD and TDC, turning the reaction mixture into a crumb during the polymerization reaction for various process conditions, as confirmed by the first set of experiments described above.

Jung teaches the addition of alkali metal and alkali earth metal halides, such as

lithium chloride and calcium chloride, as solubility-promoting additives (col. 3, lines 24-35). Jung adds these salts to keep the polymer in solution if the solubility of the polymer is too low to keep the polymer in solution without the addition of such a salt, even though such addition is not supported by experimental evidence. In Example 8 of Jung, DABI (= DAPBI) is used in a polymerization reaction performed according to the method of Example 1, i.e., without using a solubility-promoting additive. Thus, the solubility of the polymer described in Example 8 is high enough to not require the addition of a solubility-promoting additive. If nevertheless such a solubility-promoting additive is added, it would have been expected, in view of Jung's statements, that the solubility of the polymer of Example 8 would have been enhanced further.

Chernykh is similar to Jung in this respect. In Example 1 of Chernykh, 2.8% LiCl were added. This leads to a polymer solution, which can be filtered, degassed and spun to a fiber. As such, in Chernykh, LiCl has therefore been added as a solubility-promoting additive, and thus would not have been expected to lead to precipitation of the polymer.

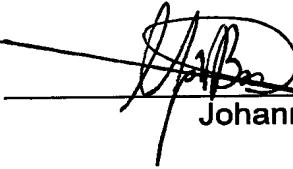
Furthermore, the Patent Office alleges that Table 2 of Chernykh describes the combination of NMP and CaCl₂. However, Table 2 of Chernykh clearly refers to Example 5 of Chernykh, which describes a benzothiazole derivative (5-amino-2-p-aminophenylbenzothiazole (DABPT)) rather than the benzimidazole derivative (i.e., DABPI), as recited in present claims 1 and 10. As the present claims are limited to the DABPI-containing aramids produced from DABPI monomeric building blocks, making a prediction that the solvent/salt combination (NMP/CaCl₂) for the DABPT-containing aramids of Example 5 would be applicable to DABPI-containing aramids is clearly unsupported by the disclosure of Chernykh.

According to the process of present claims 1 and 10, the polymer should not remain dissolved in the solvent nor precipitate from the solvent. The reaction mass should follow the same reaction path as for PPD and TDC to form PPTA, i.e. after dosing and dissolving TDC, the viscosity of the reaction mass must increase during the reaction, the flowable mixture spontaneously turns into a dough or "liquid cheese-like" material, which spontaneously becomes a crumb. Thus, if an ordinarily skilled person in the art had the objective to provide a system wherein the polymer had to be obtained as a crumb (similar to Vollbracht), he or she certainly would not have added an alkali metal or alkali earth metal salt, because Jung and Chernykh describes that such addition increases the solubility of the polymer and thus would not have been expected to produce an crumb, which is not a solution.

In view of Jung and Chernykh, it was remarkable and unexpected that the use of calcium chloride in DABPI based polymer mixtures according to the present claims does not enhance the solubility of the polymer, but to the contrary leads to the formation of an aramid crumb during copolymerization.

9. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: 24 - 3 - 2009


Johannes Bos

Translation of an article in Polimery, 1971, pp. 514-515
of Edward Chodkowski, Jan Mackowiak, Wojciech Kozlowski,
Hanna Orzechowska of Instytut Wlokienn Sztucznych i
Syntetycznych (Institute for Artificial and Synthetic
Fibres). Lodz, Pol.

Solution polycondensation of terephthaloyl chloride and
m- and p- phenylene diamine in the presence of LiCl,
LiBr and CaCl_2 .

Aromatic polyamides may be obtained by interfacial polycondensation (1) of aromatic chlorides derived from a dicarboxylic acid and aromatic diamines, or by emulsion polycondensation (2) or by polycondensation in a homogeneous medium of polar organic solvents (3).

Of the greatest interest is to be considered the polycondensation in a medium of amide solvents such as dimethyl formamide, dimethyl acetamide or N-methyl pyrrolidone, which also act as acceptors of the hydrogen chloride evolved in the reaction. In the solution polycondensation addition of an appropriate amount of some salt selected from the potassium or the calcium group to some solvents (4) makes it possible to prepare solutions of aromatic polyamides in a concentration of as high as 15-20%.

The aromatic polyamide solutions thus obtained can be used in the manufacture of films or fibres having a very high thermal resistance (5-6). Our investigations comprise the polycondensation of terephthaloyl chloride and m- and p-phenylene diamine in a medium of dimethyl acetamide at different concentrations of lithium chloride, lithium bromide or calcium chloride. In the preparation of the respective aromatic polyamides (6) considerable attention has already been paid to the use of lithium salt and other alkali metal salts, but the use for this purpose of calcium chloride is only mentioned in a few patents (4).

Experiments.

According to Coppinger (7) N,N-dimethyl acetamide was obtained from acetic anhydride and dimethyl formamide in a yield of 62% of the theoretical value. Boiling temperature 165°C at 760 mm Hg.

Terephthaloyl chloride was obtained from thionyl chloride and commercial terephthalic acid (8) in 75% yield, melting point $77^{\circ}-78^{\circ}\text{C}$ (recrystallization from petroleum ether).

Commercial m-phenylene diamine was purified by sublimation in an atmosphere of nitrogen under reduced pressure (10 mm Hg). The main fraction sublimates at a temperature of $147^{\circ}-148^{\circ}\text{ C}$. Melting point 63° C .

Commercial p-phenylenediamine was purified by sublimation in an atmosphere of nitrogen. The white acicular crystals are formed at a temperature of $140^{\circ} - 142^{\circ}\text{ C}$. Beforehand lithium chloride, lithium bromide and calcium chloride had been heated to 400° C for 2 hours.

Polycondensation was carried out in a 100-ml conical flask provided with a stirrer, thermometer, nitrogen inlet tube and a reflux condenser and an outlet tube filled with calcium chloride. After removal of the air with the aid of dry nitrogen the flask was charged with 25 ml of dimethyl acetamide and a measured quantity of LiCl, LiBr or CaCl₂, followed by stirring to obtain a homogeneous solution in which 1.458 g (0.0135 moles) of m- or p-phenylene diamine were dissolved under the same conditions. The flask was cooled to a temperature of -8° to -10°C , and over a period of 20 minutes there were gradually added, with vigorous stirring, 2.745 g (0.0135 moles) of terephthaloyl chloride, after which stirring was continued for 40 minutes. The polymer was isolated from the mixture by pouring the latter into water or methanol (500 ml), with constant stirring, followed by sucking it off through a glass Büchner funnel, washing it with methanol or acetone (in the case where it is poured into water) and subsequently drying it to a constant weight at a temperature of 110°C .

The reduced viscosity of the resulting polymers was determined from viscosity measurements, using an Ubbelohde viscometer at a temperature of 25°C, and polymer solutions in 95% sulphuric acid in a concentration of 0.5 g/100 ml of acid.

The thermal resistance of the polyamides was determined with the aid of a dynamic differential calorimeter (Perkin-Elmer DSC-1 B) and their infrared spectrum, in the range of 4000-650 cm⁻¹, was determined with the aid of a spectrophotometer (Highler & Watts Model H-800), use being made of KBr tablets.

Discussion of the results.

From the results of initial experiments in which polyphenylene terephthalamide was isolated from the reaction mixtures with the aid of water or methanol it appears that for this purpose it is far more economical to use distilled water. Polymers obtained by isolation with the aid of methanol are whiter, but the colour of the polymers isolated by means of water can be improved by rinsing the moist precipitate in acetone and subsequently drying it in an atmosphere of nitrogen, which is consequently effected very fast.

Table I.

The yield of polyphenyleneterephthalamide as a function of the precipitation medium (solution polycondensation in dimethyl acetamide without the addition of a lithium salt or calcium salt).

Name of polymer	precipitation medium	polymer yield	reduced viscosity
poly-m-phenylene-terephthalamide		65.8	0.299
		67.1	0.397
poly-p-phenylene-terephthalamide	methanol	68.2	0.300
		71.1	0.240
poly-m-phenylene-terephthalamide		39.3	0.480
		90.0	0.300
poly-p-phenylene-terephthalamide	water	91.3	0.440
		92.7	0.300

Isolating and washing polyphenyleneterephthalamide with methanol does not have any positive influence on the viscosity of this polymer, which might be expected if the low-polymeric fraction of oligomers should be soluble in this solvent (Table I)

The yield and the molecular weight of aromatic polyamides obtained by solution polycondensation are clearly influenced by the addition to the reaction medium of particular salts from the potassium group, more particularly the chloride and the nitrate of lithium (5,6).

Our investigations show that the use for this purpose of calcium chloride may lead to results similar to those obtained in the case where lithium salts are employed. The average yield of polyphenyleneterephthalamide both in the presence of a lithium salt and in the presence of calcium chloride (isolated in water and washed with acetone) is 95-98% of the theoretical value, no difference having been found between the isomeric aromatic diamines, the viscosity of the polyamides, however, is to a certain extent dependent on the nature of the isomer. The thermal characteristic of the samples of poly-m-phenyleneterephthalamide and poly-p-phenyleneterephthalamide (Table II, runs 17 and 20)

is represented in a thermogram (Fig.1) obtained with the use of a dynamic calorimeter (DSC).

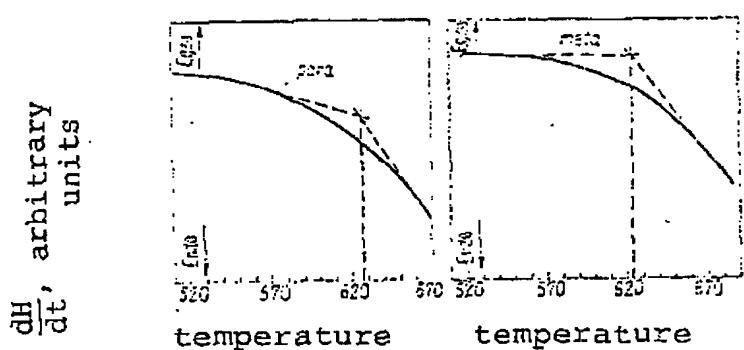


Fig.1. DSC thermograms for poly-m-phenylene terephthalamide (right) and poly-p-phenylene terephthalamide (left).

The thermograms show no sharp changes as regards the development (crystallization) or absorption (melting) of heat, which is characteristic of crystalline polymers. The smooth inflection of the thermogram curve into the endothermal direction only points to a slow thermal decomposition of these polymers, which is distinctly speeded up at a temperature $> 350^{\circ}\text{C}$. A similar characteristic is found by visual observation. For instance during the slow heating process (about $2^{\circ}\text{C}/\text{minute}$) in a capillary the meta-isomer turned yellow at a temperature of 325°C and it softened at a temperature of about 352°C , clearly displaying decomposition. The poly-m-phenyleneterephthalamides have a lower viscosity than the poly-p-phenyleneterephthalamides obtained under the same conditions in the presence of a lithium salt or a calcium salt (Table II).

Table II synthesis of poly-m- and p-phenyleneterephthalamides.

Name of diamine		Salt type and concentration		Reduced viscosity η_r	
		concentration			
		mole/l	%		
m-phenylenediamine	-			0.240	
	-			0.300	
p-phenylenediamine	-			0.440	
	-			0.315	
m-phenylenediamine	LiCl	0.50	2.12	0.460	
	"	0.75	3.18	0.379	
	"	1.00	4.24	0.338	
p-phenylenediamine	"	0.50	2.12	0.750	
	"	0.75	3.18	0.420	
	"	1.00	4.24	0.338	
m-phenylenediamine	LiBr	0.50	4.34	0.610	
	"	0.75	6.51	0.473	
	"	1.00	8.69	0.360	
	"	0.50	4.34	0.808	
p-phenylenediamine	"	0.75	6.51	0.555	
	"	1.00	8.69	0.372	
	"			4.11	
m-phenylenediamine	CaCl ₂	0.50	5.55	1.413	
	"	0.75	8.33	0.718	
	"	1.00	11.10	0.340	
p-phenylenediamine	"	0.50	5.55	1.539	
	"	0.75	8.33	1.273	
	"	1.00	11.10	0.497	

The infrared spectra of the isomeric aromatic polyamide samples are very much alike. Differences in absorption are only found in the range of $900-750\text{ cm}^{-1}$.

Poly-m-phenyleneterephthalamide shows an intensive band in the vicinity of 850 cm^{-1} , poly-p-phenyleneterephthalamide, however, in the neighbourhood of 755 cm^{-1} , which is characteristic of the position of meta and para. Comparing the two spectra, we can establish that the peaks at the right of the spectrum of poly-p-phenyleneterephthalamide have shifted towards higher wave lengths than the isomeric m-polymer (Fig.2)

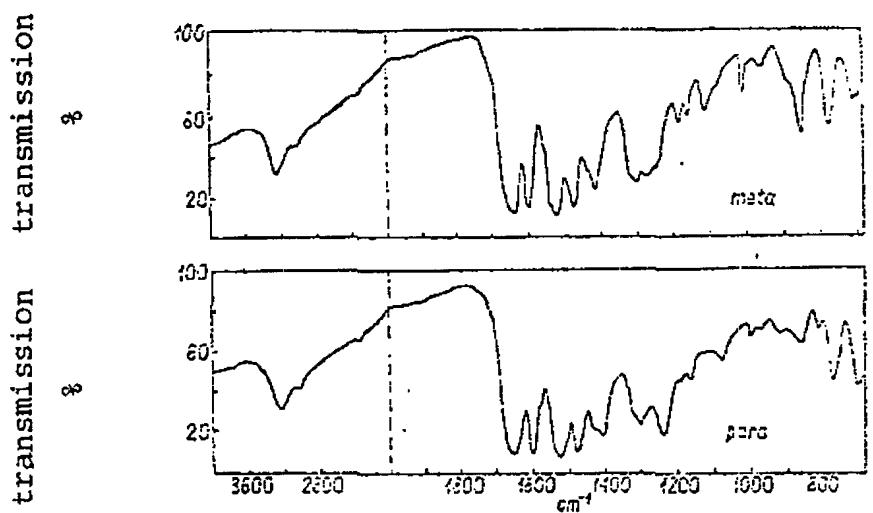


Fig. 2 Infrared spectrum of poly-m-phenyleneterephthalamide (top) and poly-p-phenyleneterephthalamide.

Acknowledgement is due to Prof. Dr. T.Skwarski for his interest in and discussion of the subject.

Literature.

1. Dine Hart A., Moor J., Right W.: *J. Polymer Sci.* B 2 360 (1964).
2. Sokolow L.B., Kudin T.W.: *Dan SSSR* 158, 1139 (1964).
3. British patent 871 578 (1961)
4. British patent 871 580, 871 581 (1961).
5. Sawinow W.M., Sokolow L.B.: *Chim. Włókna* 4, 22 (1965)
6. Fiodorow A.A., Sokolow L.B., Sawinow W.M., Lukianienko I.G.: *Wysokomol. Sojed* B 11, 129 (1969)
7. Rugli H., Kuecht R.: *Helv. Chim. Acta* 39, 4857 (1945)

Received on 1970-07-25.